

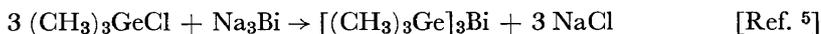
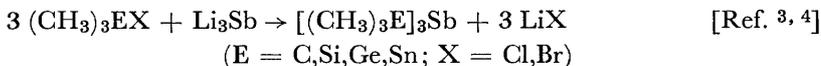
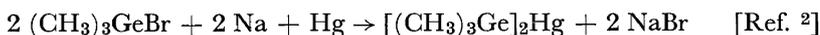
ORGANOSILICON AND ORGANOGERMANIUM DERIVATIVES WITH SILICON—METAL AND GERMANIUM—METAL BONDS

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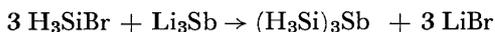
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In recent years, interest has grown in the chemistry of bimetallic organometallic compounds containing metal-metal bonding between atoms of different metals. Compounds of this type are very different in their chemical properties from the "ordinary" organometallic compounds. In this connection it is interesting to compare the reactivity of the bimetallic organometallic compounds with that of the correspondin "ordinary" (*i.e.* without Si-metal or Ge-metal bonds) organometallic compounds, although our data on the chemical properties of the former are far from being complete.

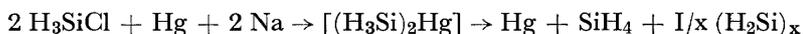
Silyl and germyl halides, which are instantaneously acted upon by two metals, one of which is a halogen acceptor and the other being a fixative metal of the organosilyl or organogermyl radicals, are used for the preparation of bimetallic organometallic compounds:



Synthesis of compounds containing As-Si, As-Ge and related linkages proceeds similarly⁴. It is to be noted that the yields of tris(trimethylmetal IV)antimony and tris(trimethylmetal IV)arsenic compounds are found to be rather high (80–85 per cent). Poor results have been obtained when applying this method to the synthesis of the "ordinary" organometallic compounds. For example, when *t*-butyl chloride is allowed to react with Li₃Sb, the yield of tri-*t*-butylantimony falls to approximately 1 per cent.^{3, 4} The above-mentioned reactions were used for the preparation of (H₃Si)₃Sb⁶:



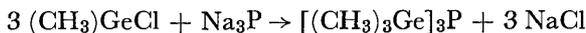
Attempts to synthesize (H₃Si)₂Hg from chlorosilane and sodium amalgam resulted in decomposition of the reaction mixture⁷ with formation of mercury, silane, and the polymer (H₂Si)_x:



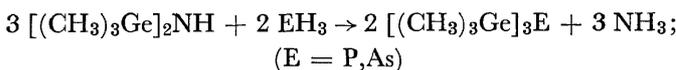
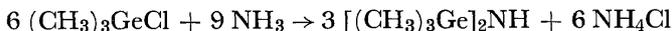
Attempts to prepare bis(dimethylsilyl)mercury and bis(methylsilyl)mercury were also unsuccessful¹. These compounds proved to be unstable. They

immediately decompose to give mercury and the products of disproportionation and dimerization of the organosilyl radicals. It is noteworthy that bis(trimethylsilyl)mercury appears to be a very stable compound, decomposing on heating. The replacement of a methyl radical in the $(\text{CH}_3)_3\text{Si}$ group by hydrogen gives an extremely labile structure.

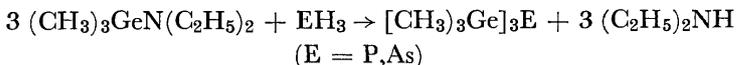
Germyl-phosphorus and germyl-arsenic derivatives can be prepared according to⁸:



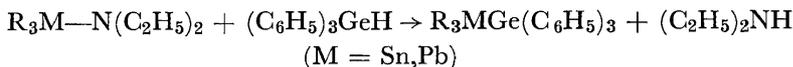
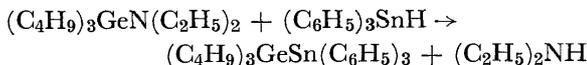
The reaction takes place in liquid ammonia, which participates insofar as this reaction does not occur in ether. It may be suggested that the interaction of ammonia with trimethylchlorogermane yields hexamethyldigermazane which reacts with a free phosphine or arsine:



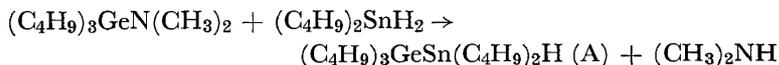
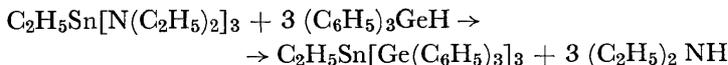
It is advisable to use organogermanium-nitrogen compounds for the synthesis of Ge-P and Ge-As bonds. In this case the reaction can be carried out in an ethereal solution⁸:



Recently the hydrogenolytic fission of Sn-N^{9, 10, 10a, 10b}, Ge-N^{9, 10}, and Pb-N^{10c} bonds with organotin or organogermanium hydrides was recognized as an important method for the preparation of tin-germanium and lead-germanium compounds. For example:



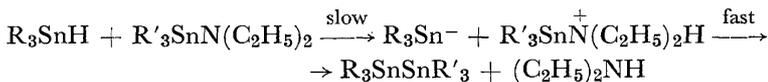
By this method a number of linear and branched compounds with Ge-Sn bonds have been prepared. For example:



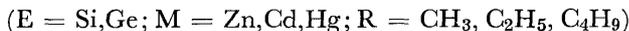
Upon catalytic decomposition of this hydride under the influence of diethylamine a linear tetrametal derivative is formed:



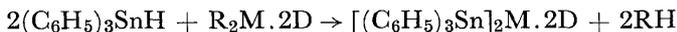
The mechanism of these reactions is illustrated by the example of the synthesis of ditin compounds^{10, 11}



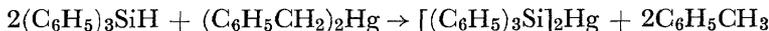
Vyazankin, Razuvaev *et al.*¹²⁻¹⁶ reported on the reactions of the triethyl hydrides of the group IV^b elements with ethyl derivatives of mercury, cadmium and zinc, yielding compounds of the general formula $[(\text{C}_2\text{H}_5)_3\text{E}]_2\text{M}$ (where E = Si, Ge; M = Hg, Cd, Zn):



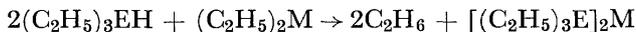
Compounds with the Sn—Zn and Sn—Cd bonds can be prepared in this way only under the action of organotin hydrides on the dialkylmetal compounds in a complexing solvent (tetrahydrofuran, dimethoxyethane), or by using a preformed co-ordination complex of R_2M , *e.g.* with *o*-phenanthroline, 2,2'-bipyridyl or N,N,N',N'-tetramethylethylenediamine^{10, 17}:



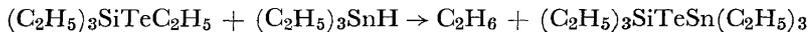
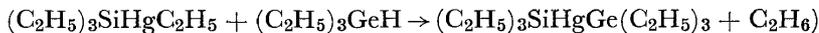
In the absence of complexing agents (D) these compounds are unstable and only their decomposition products have been isolated. In order to prepare a bis(triphenylsilyl)mercury, dibenzylmercury can conveniently be used¹⁸:



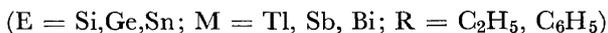
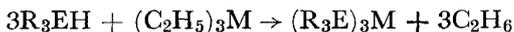
Pentaethyldisilane reacts with diethylmercury to give compounds with the Si—Si—Hg—C—C and Si—Si—Hg—Si—Si linkages¹⁹. When diethylselenide (or diethyltelluride) was allowed to react with the triethyl hydrides of the group IV^B elements, stannyl derivatives, in addition to the silyl and germyl ones, were obtained^{20, 21}:



In the reactions under investigation incompletely substituted compounds of the type $(\text{C}_2\text{H}_5)_3\text{E—MC}_2\text{H}_5$, (where E = Si, Ge; M = Hg, Se, Te), are formed simultaneously with symmetrical products. Using the latter, some mixed derivatives can be prepared. For example^{16, 19, 21}:



Recently it was found that organic hydrides of the group IV^B elements react with triethylthallium^{22, 61}, triethylantimony and triethylbismuth^{10, 23-26}



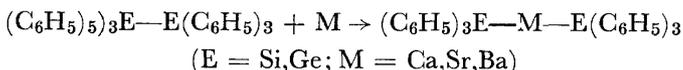
These reactions also proceed stepwise and in several cases the unsymmetrical products can be obtained, *e.g.* $(\text{C}_2\text{H}_5)_3\text{GeBi}(\text{C}_2\text{H}_5)_2$, and $[(\text{C}_2\text{H}_5)_3\text{Ge}]_2\text{BiC}_2\text{H}_5$ ²⁶.

Attempts to prepare compounds with Si—Sn and Ge—Sn bonds by heating triethylsilane or triethylgermane with tetraethyltin were unsuccessful. Treatment of triethylsilane and its isologues with tetraethyllead yielded intermediate compounds with Si—Pb, Sn—Pb and Ge—Pb bonds²⁷.

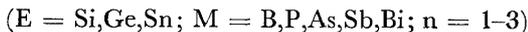
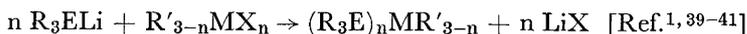
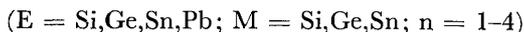
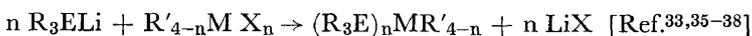
Syntheses of bimetallic organometallic compounds can be carried out by the cleavage of compounds of the type $\text{Ar}_3\text{E—EAr}_3$, (where $\text{E} = \text{Si, Ge, Sn, Pb}$), with alkali and alkali-earth metals. The preparation of organosilyl alkali metal compounds has been reviewed in detail^{28, 29}. In these syntheses the solvent seems to be of extreme significance. For example, triphenylsilylsodium can be prepared by the cleavage of hexaphenyldisilane with sodium in 1,2-dimethoxyethane³⁰ or in liquid ammonia¹ but not in an etheral medium. High yields of triphenylsilylsodium in THF are obtained in presence of naphthalene or biphenyl³². Although hexaalkyl compounds with Sn—Sn and Pb—Pb bonds can be split by alkali metals to give the alkali metal salts³¹, the corresponding compounds of germanium and silicon seem to be resistant to cleavage by alkali metals in common solvents. Hexamethylphosphortriamide is said to be an excellent solvent. A quantitative reaction occurs in it at normal temperature³³:



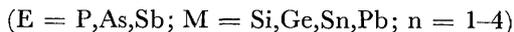
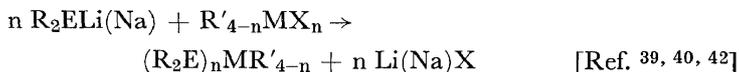
Alkali-earth metals are capable of cleaving the silicon-silicon¹ and germanium-germanium bonds³⁴ in liquid ammonia solution:



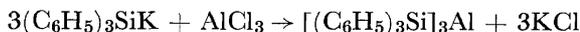
A variety of bimetallic compounds have been prepared in the reactions of metal halides with the alkali metal derivative of another metal:



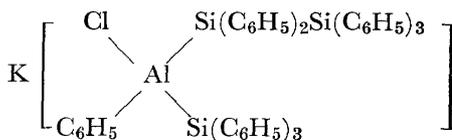
In several cases with the same end in view, derivatives are used in which the alkali metal is bonded with an element of group V of the periodic table:



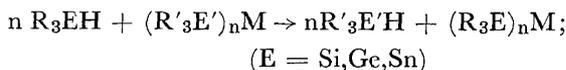
It is interesting to note that in the preparation of tris(triphenylsilyl)aluminium:



the resulting aluminium compound rearranges and gives a complex of the following structure with potassium chloride¹:

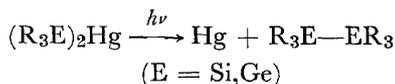


Compounds of the type $(\text{R}_3\text{E})_n\text{M}$ with silicon-metal and germanium-metal bonds can also be obtained by metal exchange reactions as well as by the replacement of R_3E radicals according to the equation:

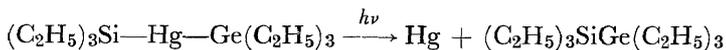


These reactions will be discussed below.

In this paper we shall not report on the reactivity of bimetallic organo-metallic compounds in which a group IV^B element is attached to an alkali metal. There are special reviews on this subject^{28, 29}. In addition, they differ considerably in their properties from the derivatives of other metals. Silyl-, germyl- and stannyl-metallic derivatives are sensitive to light. They are decomposed under ultraviolet light in molybdenic reaction tubes. As a rule, under comparable conditions the "ordinary" organometallic compounds are not decomposed. For example, compounds in which a group IV^B element is attached to strontium, barium³⁴, zinc¹², mercury^{1, 15, 16, 18, 19, 43}, or stibium³ are decomposed under the light. Photolysis accompanied by a quantitative decomposition according to the equation cited below has been investigated in some detail for mercury compounds



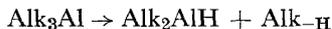
Photolytic decomposition proceeds molecularly without a noticeable production of free R_3E radicals. Such a mechanism is pointed to by formation of mercury and triethylsilyltriethylgermane from the photolysis of triethylsilyl (triethylgermyl) mercury¹⁹:



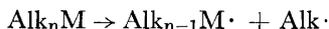
If free silyl and germyl radicals were to be formed, hexaethyldisilane and hexaethyldigermane would have also been produced. In addition, when bis (triethylgermyl)mercury was decomposed in cumene, tetraethyltin or *t*-butyl peroxide in the absence of oxygen with ultraviolet light, the products were mercury and hexaethyldigermane. Triethylgermane was not detected¹⁶. The presence of this compound would have been expected if hydrogen abstraction by triethylgermyl radicals from the solvents had occurred. The photochemical decomposition of "ordinary" organometallic compounds has been studied extensively⁴⁴. Many of these reactions were interpreted as radical processes involving disproportionation and dimerization of the resulting radicals, induced decomposition of the starting organo-metallic compound and interaction of the radicals with the solvent.

Thermal decomposition of "ordinary" organometallic compounds proceeds via two routes:

(a) The decomposition of organometallic compounds of alkali metals, aluminium *etc.* gave derivatives with metal-hydrogen bonds⁴⁵:



(b) Free radical decomposition of organo-mercury, -tin, -lead and related compounds:



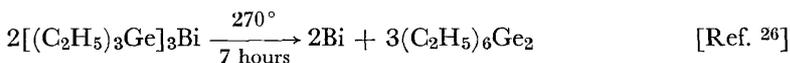
Alkyl radicals may then react further by disproportionation, by dimerization and by hydrogen abstraction from the unreacted organometallic compound:



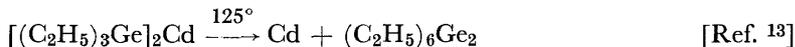
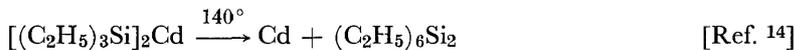
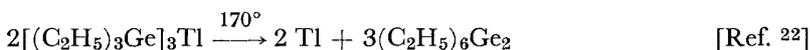
The secondary radical of the type $\text{Alk}_{n-1}\text{MAlk}\cdot\text{-H}$ is often decomposed:



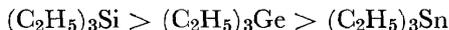
Thermal decomposition of bimetallic organometallic compounds proceeds most often with the deposition of a metal and dimerization of the radicals attached to it:



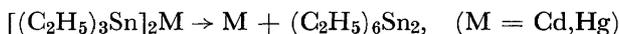
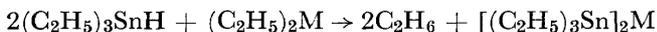
Tris(trimethylgermyl)bismuth is decomposed in a similar way but under more mild conditions⁶.



Mercury compounds are heat-resistant. For example, bis(trimethylgermyl)mercury, when heated to 160° for 19 hours, is decomposed by ~ 10 per cent¹⁵. While comparing the thermal stability of the compounds $[(\text{C}_2\text{H}_5)_3\text{E}]_3\text{M}$ (where $\text{M} = \text{Sb}, \text{Bi}$), it has been discovered that it decreases in the order²⁴:



The thermal stability of cadmium and mercury derivatives follows the same order of decrease. For example, compounds with Sn-Cd-Sn and Sn-Hg-Sn bonds will not be isolated when diethylcadmium and diethylmercury are acted upon by triethyltin hydride. They are decomposed during synthesis to cadmium (or mercury respectively) and hexaethyltin⁴⁶:

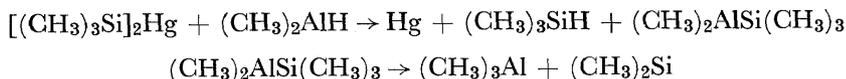


Free radical decomposition is observed with trialkylsilyl mercury and stibium derivatives. On a prolonged heating of bis(trimethylsilyl)mercury

which decomposes according to the equation:



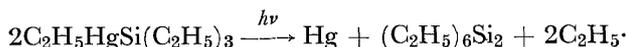
The interaction of dimethylsilene with bis(trimethylsilyl)mercury gives $(\text{CH}_3)_3\text{Si} [(\text{CH}_3)_2\text{Si}]_n\text{Si}(\text{CH}_3)_3$, (where $n = 1, 2$). Trisilane and tetrasilane are formed in a similar reaction with dimethylaluminium hydride¹:



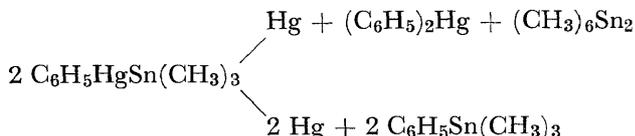
Asymmetric compounds of the $\text{C}_2\text{H}_5\text{HgSi}(\text{C}_2\text{H}_5)_3$ type are stable enough. They are distilled in vacuum without decomposition. On heating to 170° a disproportionation reaction occurs¹⁹:



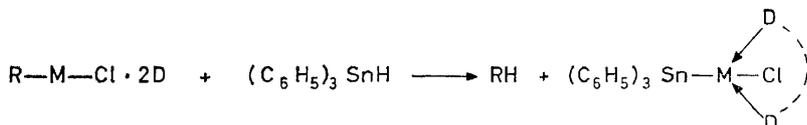
Photolytic decomposition proceeds to give hexaethylidisilane¹⁶:



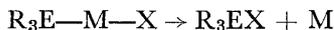
It has been indicated that phenyl(trimethylstannyl)mercury is decomposed as it is formed via two routes⁴⁹:



Triphenylstannylmetal chloride complexes of the type $\text{Ph}_3\text{SnMCl} \cdot 2\text{D}$ were obtained by the reaction of EtZnCl or MeCdCl , either in the solvated form or as a pre-formed complex, with triphenyltin hydride at -40° ^{10, 17}:

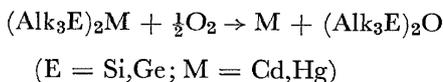


In other cases when compounds of the type $\text{R}_3\text{E}-\text{M}-\text{X}$, (where $\text{E} = \text{Si}, \text{Ge}$; $\text{X} = \text{halogen, alkoxy}$ and related electro-negative groups), have to be formed, the decomposition products only can be identified in the reaction mixture:

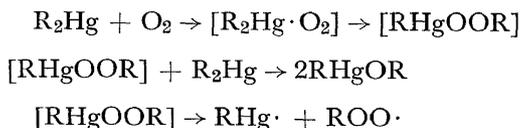


Many compounds of the $(\text{R}_3\text{E})_n\text{M}$ series (where $\text{E} = \text{Si}, \text{Ge}, \text{Sn}$; $\text{M} = \text{non-transition metal of II-VI groups}$) are readily oxidized. With $\text{R} = \text{alkyl}$ these reactions proceed more rapidly than that with $\text{R} = \text{aryl}$. As for the oxidation products, the bimetallic organometallic compounds can be divided into two groups: (a) those oxidizing with the deposition of the metal M and (b) those oxidizing without it. It should be pointed out that there is still very little information on the oxidation reactions. In the majority of cases they are said to be extremely sensitive to oxygen. No attempts to clarify the nature of the products formed has been made. Oxidation of cadmium¹³

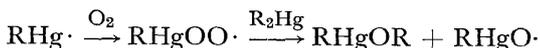
and mercury^{15, 16} derivatives proceeds to give a quantitative formation of hexaalkylsiloxanes or hexaalkylgermoxanes:



For mercury compounds this reaction has been investigated in more detail. It should be particularly emphasized that there is some difference in oxidation mechanism of the "ordinary" organomercury compounds and that of the organometallic compounds with metal-mercury bonds. The oxidation of mercurials (*e.g.* di-isopropylmercury, dicyclohexylmercury) proceeds involving a free radical-chain mechanism⁵⁰. Initially, oxygen attacked the mercurial to form the unstable intermediate organomercury peroxide, [RHgOOR]. The peroxide reacted with unoxidized mercurial to give a compound of the type RHgOR, or partially decomposed into a peroxyalkyl radical, ROO· and alkylmercury radical, RHg·:



Alkylmercury radicals also oxidized to give the RHgOO· radicals. The latter reacted as an oxidizing agent with mercurial:

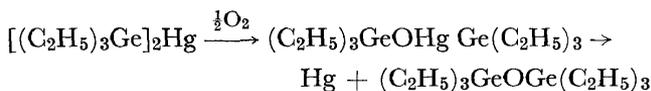


The alkoxy derivative reacted with oxygen or partially decomposed into the free radicals

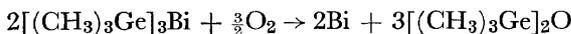


In the presence of moisture the alkoxy compound is easily hydrolysed to the stable hydroxide. Therefore, a small addition of water to the reaction mixture decreases considerably the rate of oxidation of the organomercury compounds. The addition of the radical scavenger also decreases the rate of these reactions. If oxidation is to be carried out in nonane medium, the latter undergoes some oxidation.

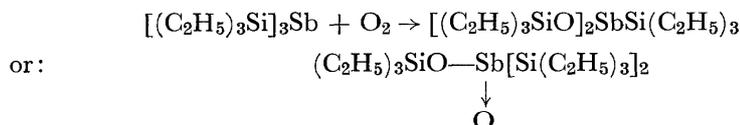
Bis(triethylgermyl)mercury is autooxidized in nonane solution which, in turn, remains unchanged. The rate of reaction is not dependent upon addition of radical inhibitors. Under normal conditions every mole of starting germyl mercuric derivative requires at least 0.5 mole of oxygen. The reaction results in the formation of hexaethylgermoxane and metallic mercury, the yields of which are quantitative. If oxidation, however, is to be carried out at low temperatures, for example at -20° , only a part of mercury precipitates as metal, the remainder appears to be present in the solution in the form of an unstable product decomposing at room temperature (even in the absence of oxygen) to mercury and hexaethylgermoxane. It can be suggested on the basis of material equilibrium that the unstable product possesses the same structure as triethylgermyl(triethylgermyloxy)-mercury⁵¹:



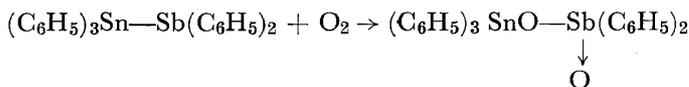
It might be that the peroxide which oxidizes the germylmercury compound, not having entered into the reaction to the said oxide, is formed firstly. It is well in agreement with the fact that the oxidation of bis(triethylgermyl)mercury at -50° in nonane in the presence of ammonia proceeds to give $(C_2H_5)_3GeOGe(C_2H_5)_3$. The investigation of autooxidation kinetics has shown that triethylgermoxane catalyzes the process. Catalytic action is also disclosed by ammonia, amines and triphenylphosphine. Of the germyl compounds of group V elements, tris(trimethylgermyl)bismuth is oxidized to give a metal⁵:



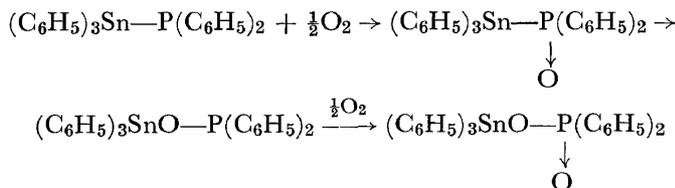
Organobimetallic antimony compounds are oxidized to yield the oxidation products. No metal can be detected among the products. For example, tris-(triethylsilyl)antimony is oxidized in hexane solution at normal temperature according to the equation²⁴:



The above cited formula is in good agreement with the product formed during the oxidation of stannyl-antimony derivative⁴⁰:



The oxidation mechanism is illustrated by the example of the phosphorus analogue⁷⁰:

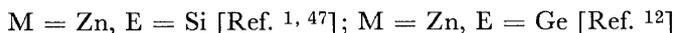
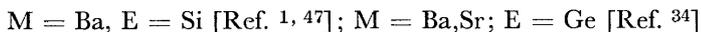
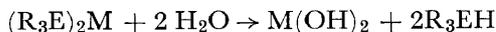


Silyl derivatives of the type $R_3Si-AsR_2$, $R_3Si-SbR_2$ and R_3Si-PR_2 are very easily oxidized.

The description of the hydrolysis of silyl and germyl metallic compounds is far from being complete. With respect to the effects of water, these compounds can be divided into three broad groups:

- (a) those which do not interact with water;
- (b) those hydrolysing to give hydroxides of metals and organohydrides of silicone or germanium;
- (c) those hydrolysing to isolate a metal in its free state and the mixture of R_3EH and R_3EOH .

Among the derivatives of the metals of group II, the mercury compounds are known to be stable to water. The compounds of alkali-earth metals and those of zinc react with water in the same manner as the "ordinary" organometallic compounds *i.e.* to give $M(OH)_2$ according to the equation:



Rapid hydrolysis is accompanied by a slower reaction³⁴:



which can be accelerated by acidifying the aqueous solution¹.

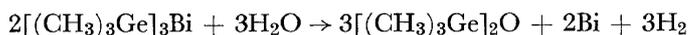
Behaviour of cadmium derivatives is somewhat different. Upon the hydrolysis of bis(triethylgermyl)cadmium, the metal can be identified among the products¹³:



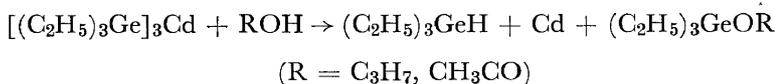
Hydrolysis of thallium compounds also proceeds to give the metal²²:



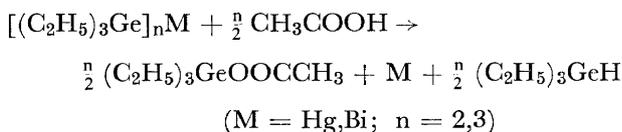
It has been indicated that the compounds of the series $[(CH_3)_3E]_3Sb$ (where $E = C, Si, Ge, Sn$), are sensitive to the presence of water³. Hydrolysis of tris(trimethylgermyl)bismuth proceeds according to the equation⁵:



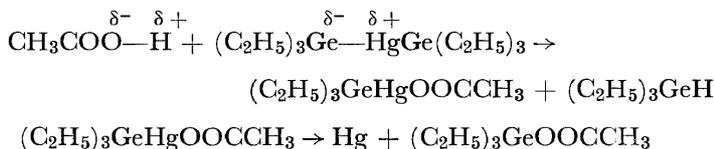
The reactions of germyl cadmium derivatives with alcohols and acetic acid proceed similarly to hydrolysis⁵²:



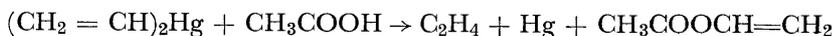
Mercuric²⁶ and bismuth²⁴ derivatives stable to hydrolysis can also react with acetic acid:



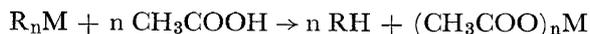
It is quite naturally to be assumed that the intermediate products of acidolysis are the unstable mixed organobimetallic compounds, the decomposition of which, as cited previously, proceeds to give a free metal. For example:



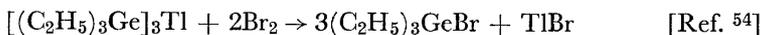
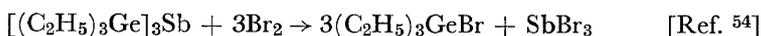
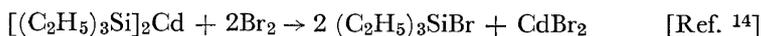
Among the "ordinary" organomercuric compounds divinylmercury reacts with acetic acid in a similar way⁵³:



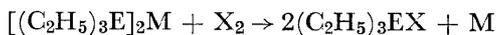
In the majority of cases, however, the "ordinary" organomercuric and organobismuth compounds react with acetic acid accompanied by a hydrocarbon abstraction and the formation of metallic acetates. The resulting mixed organometallic acetates are found to be stable and do not undergo any decomposition:



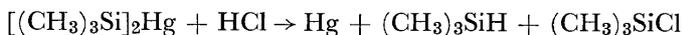
The action of halogens on silyl and germyl metallic derivatives is similar to that of the "ordinary" organometallic compounds *i.e.* the rupture of the metal-radical linkage is observed:



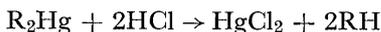
Selenium and tellurium derivatives are characterized by giving free Se or Te⁵⁴:



As far the action of hydrogen chloride is concerned, (which is known for mercuric derivatives only), the reaction with bis(trimethylsilyl)-mercury proceeds to give the metal¹:



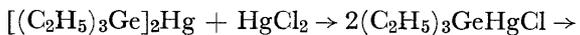
while the "ordinary" organomercuric compounds react with the same reagent abstracting a hydrocarbon according to the equation:



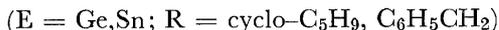
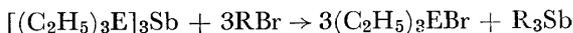
Reactions of organometallic compounds with the halogen products of the same metals which result in the formation of organometallic halogens are of great value. This process is widely used in the synthetic chemistry of organometallic compounds. For example, for the mercuric compounds this reaction runs according to the equation:



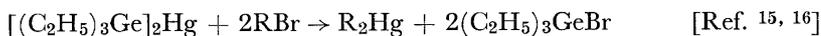
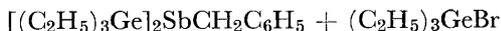
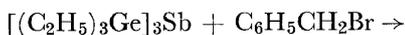
As for the organobimetallic compounds of mercury, their interaction with HgCl_2 proceeds to give heat and metallic mercury. Their action in the first step also results in the formation of a mixed compound which is unstable and decomposes as follows⁵⁵: (see also Note added in proof on p. 374)



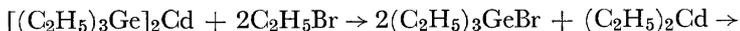
Organic monohalogen derivatives react with organobimetallic compounds on heating or under ultraviolet irradiation in the orientation of the metal-silicon or metal-germanium bond. The halogen atom of the reacting compound is added to the silicon or germanium, and the organic radical to the central metal atom^{23, 24}:



With the reagent ratio 1:1, the partially substituted product is formed:

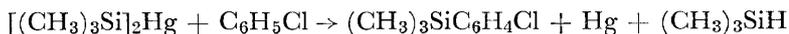


In several cases when an organometallic compound with high reactivity is to be formed, it can react with the resulting halogen derivative:

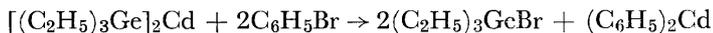


It is of interest to note that the reaction of bis(triethylgermyl)mercury with bromobenzene can be initiated by oxidation¹⁵. Diphenylmercury and triethylbromogermane are yielded as well as some amount of oxidation products, namely hexaethylgermoxane and mercury. A similar reaction proceeding in fluorobenzene solution resulted in the formation of oxidized products only. The solvent did not participate in the reaction¹⁵.

A somewhat different reaction occurs between bis(trimethylsilyl)mercury and chlorobenzene at high temperature. The trimethylsilyl radical enters the aromatic nucleus⁴⁷:

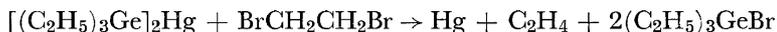


Bis(triethylgermyl)cadmium when heated for a long period of time in bromobenzene solution did not react with the latter. Hexaethyldigermane and cadmium can be identified only among the reaction products. Under ultraviolet irradiation the interaction of the reaction mixture with the solvent proceeds at 40 per cent complete⁵⁶:

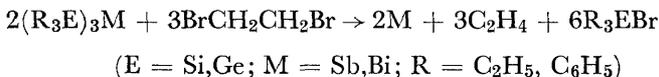


The resulting compounds partially reacted with one another in a slower manner to form cadmium bromide and triethylphenylgermane.

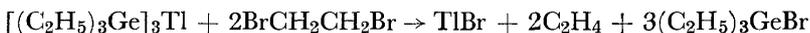
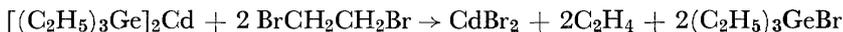
The reaction of organobimetallic compounds with 1,2-dibromoethane is somewhat peculiar. As a result of exothermal reaction mercuric compounds give some quantitative yields of the products according to the equation¹²:



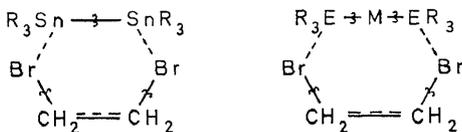
On heating the reaction of stibium and bismuth derivatives occurs with some difficulty. It proceeds quantitatively according to the equation^{23, 24, 27}:



Sometimes the exothermal reactions take place between the resulting metal and 1,2-dibromoethane¹³:

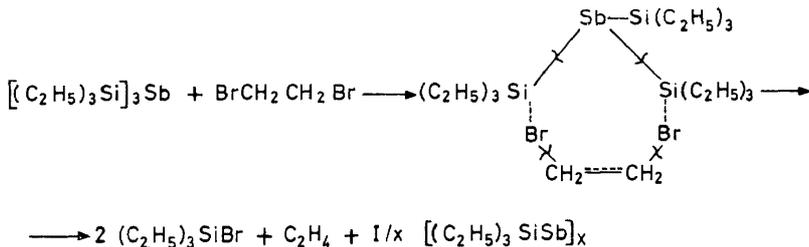


Reactions with 1,2-dibromoethane are similar to those of hexasubstituted ditin compounds and diplumbanes as well as triphenyllead-lithium^{57, 58}. The reaction appears to involve a formation of intermediate cyclic complexes:



which are decomposed to give ethylene and R₃EBr (where E = Si, Ge).

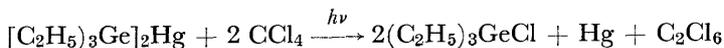
Such a suggestion is confirmed by the reaction of tris(triethylsilyl)antimony with 1,2-dibromoethane in the reactant ratio 1:1. The intermediate cyclic complex is decomposed to give a polymeric triethylsilylantimony²³:



Reactions of organobimetallic compounds with carbon tetrachloride proceed under much more complicated conditions. These have only been investigated in the case of mercury and cadmium derivatives. The "ordinary" organo-mercuric compounds enter into the reaction with CCl₄ under ultraviolet irradiation according the equation:



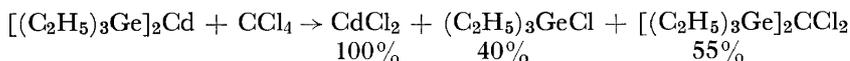
Bis(triethylgermyl)mercury also reacts with CCl₄ under ultraviolet irradiation to form metallic mercury¹⁵:



It is very likely that in this case, too, a mixed compound is formed first and then decomposes to give the metal:

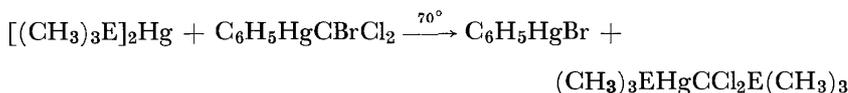


The corresponding cadmium derivative reacts with CCl_4 at normal temperature with an explosion. At -75° the following products are observed⁵⁶:

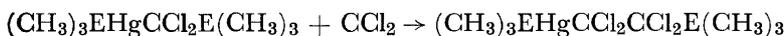


A high yield of the last product allows a suggestion to be made concerning the fact that dichlorocarbon is formed in the course of the reaction which is known to be characteristic of the insertion reactions into molecules of the organometallic compounds.

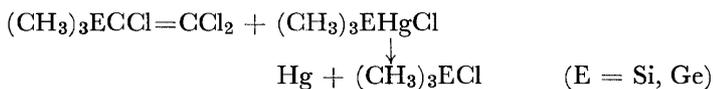
Such an insertion reaction has been described for silyl and germyl mercury derivatives. As a source of dichlorocarbon, the thermal decomposition of trihalogenmethyl-mercury compounds was used⁵⁵:



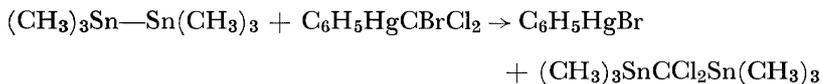
The dichlorocarbon insertion reaction proceeds much further towards completion:



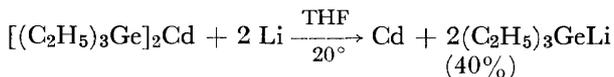
The resultant compound decomposes giving:



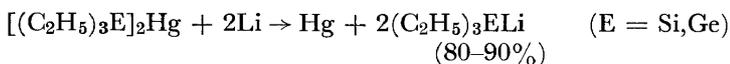
The ability of dichlorocarbon to be inserted in the orientation of the metal-metal bond is demonstrated using the reaction with hexamethylditin during which a stable insertion product is being formed⁴⁹:



The reaction common to all organometallic compounds is the transfer of radicals from one organometallic compound to another metal. Organobimetallic compounds are considered to be convenient material for the preparation of silyl and germyl lithium compounds. Such transfers are described for cadmium compounds⁵⁶:

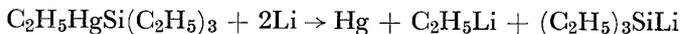


Mercuric derivatives can be readily used for synthesis⁵⁹:

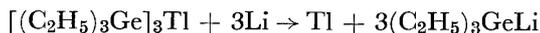


When an incompletely substituted silyl mercury derivative is acted upon

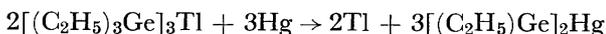
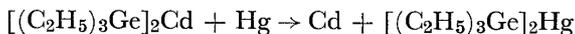
by lithium, a mixture of lithium compounds can be obtained at the expense of the transfer of both the radicals to lithium³⁸:



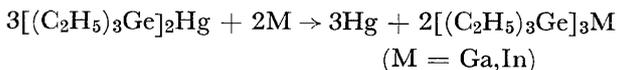
The radicals of mercuric compounds are also transferred to sodium⁵⁶. Triethylgermyllithium can be prepared by a lithium attack on tris(triethylgermyl)thallium⁶⁰:



The radicals from cadmium⁵² and thallium^{22,61} compounds are transferred to mercury:

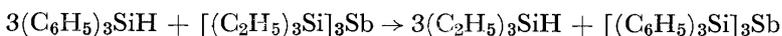


This method can be used for preparation of germyl-gallium and -indium compounds:



Bis(trimethylsilyl)mercury was used for the preparation of silyl aluminium derivatives. The tris(trimethylsilyl)aluminium formed as a result of the radical transfer proved, however, to be an unstable compound decomposing under the conditions of synthesis¹.

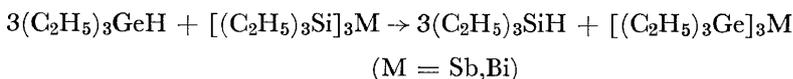
Another reaction which can be successfully used for the purpose of synthesis is the reaction of radical displacement from organobimetallic compounds by the hydrides of other elements of group IV. The less active hydrides are displaced by those which are more active. Such reactions can take place with hydrides of the like element as that of the radical linked with the metal, for example^{23,24}:



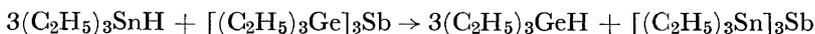
If an organometallic compound is acted upon by a hydride of approximately the same activity as that of the radical linked with the metal, an equilibrium is set up:



Germanium organohydrides are more reactive than those of silicon. They are capable of displacing triethylsilane from stibium and bismuth derivatives:

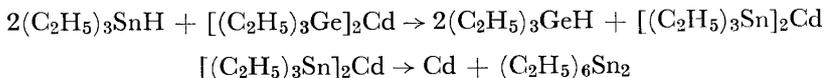


Organotin hydrides which can displace the germyl radical proved to be more active:

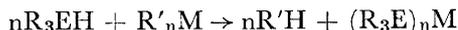


Tris(triethylgermyl)bismuth also enters into the reaction with triethyltin but the resulting compound is found to be unstable and decomposes under

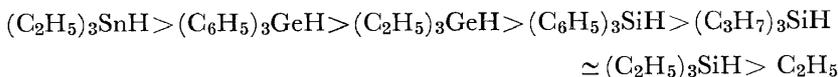
experimental conditions to give bismuth and hexaethyliditin²³. The same is observed with mercury and cadmium compounds⁵²:



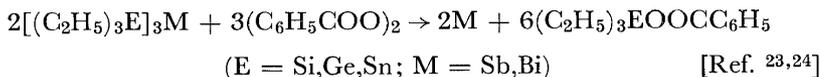
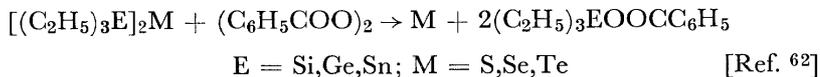
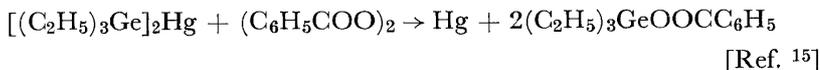
The method used for the preparation of organobimetallic compounds represents a particular case of the displacement reaction of the carbon radical:



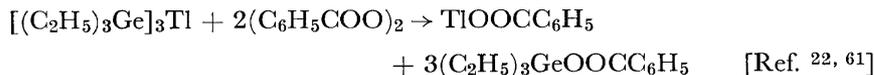
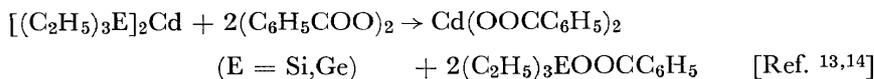
As to their reactivity, the hydrides can be arranged in the following succession²⁴:



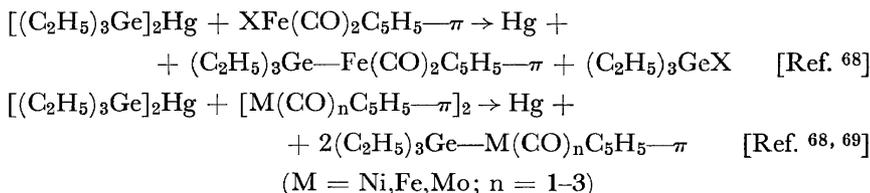
Some special attention should be paid to the reactions proceeding between organobimetallic compounds and peroxides. *t*-Butyl peroxide does not enter into the reaction under normal conditions¹⁶. As far as acyl peroxides are concerned, their reactions with organobimetallic compounds proceed smoothly resembling the reactions with 1,2-dibromoethane in spite of the quite different nature of the reactants. Those organometallic compounds in which the reaction with 1,2-dibromoethane is found to be exothermal can react with acyl peroxides, as well. In those cases where a free metal or element is isolated in the reaction with 1,2-dibromoethane, a somewhat similar reaction with the peroxides takes place:



In those cases where metal is isolated as bromide, a metal salt is formed in addition to acyl peroxide:



As with 1,2-dibromoethane, the reactions of organobimetallic compounds with acyl peroxides are similar to those of peroxides with hexaethyliditin⁶³ or hexaethyldiplumbane⁶⁴. The latter react with benzoyl peroxide to give a quantitative formation of triethyltin or triethyllead benzoates. It is



This scant information on the application of highly reactive organobimetallic compounds shows that there is no doubt that they are worthy of serious note. The routes for their application are peculiar so that studies on their properties and the expansion of investigations in the field of synthesis of organobimetallic compounds, with new metal-metal groupings, need to be performed in some detail.

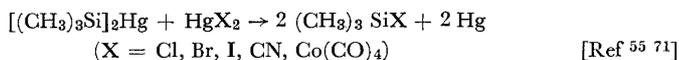
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Note added in proof

The reaction of bis(trimethylsilyl)mercury with a variety of mercuric compounds goes in a similar manner



The reaction of organobimetallic compounds with organomercuric halides has considerable possibilities for the synthesis of compounds with Si-Hg-C and Ge-Hg-C groupings

